Correlating AFM Probe Morphology to Image Resolution for Single Wall Carbon Nanotube Tips

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Supporting Information:

Nanotube AFM Tip Attachment

Methods we compared for attaching nanotubes to silicon AFM tips include manual assembly, direct growth and pickup.

Smalley's group reported the first example of the use of carbon nanotubes as AFM tips in 1996.[1] They manually attached multi-wall carbon nanotubes (MWNT) and ropes of individual SWNTs to the apex of silicon pyramidal tips using tape adhesive and a micromanipulator in an optical microscope. The main drawback to this method is that MWNT tips large enough to be seen optically did not improve the resolution much beyond standard silicon tips when imaging isolated amyloid fibrils.[2]

We found it fairly efficient to manually attach MWNTs to silicon AFM cantilevers with a 1000x optical microscope. In particular, the rate of assembly was quite high when a 15 V potential was applied between the silicon probe and the nanotubes. This resulted in nearly perfect and rapid alignment of the nanotube to the silicon tip. However, there was not a clear path to doing so with the thin SWNTs required for very high-resolution imaging.

Lieber[3,4] and Quate's[5] groups later showed that individual single wall carbon nanotubes could be directly grown by chemical vapor deposition (CVD) on the silicon tips themselves by first pre-coating the tip with a metal catalyst. In the CVD synthesis of carbon nanotubes, metal catalyst nanoparticles are heated in the presence of a hydrocarbon gas or carbon monoxide; the gas molecules dissociate on the catalyst surface and carbon is adsorbed into the particle. As the carbon precipitates, a carbon nanotube is grown with a diameter similar to that of the catalyst particle.

Two techniques for direct growth have been reported. One involves creating nanopores at the apex of the silicon tip by etching with hydrofluoric acid. Catalyst particles are then deposited inside the nanopores. Carbon nanotubes grown via CVD from such a tip have an appropriate geometry for AFM imaging. While this approach enables fabrication of SWNT tips, the preparation of the porous layer in the silicon is time consuming and placement of the nanotube at the optimal location near the tip apex is

often not achieved. In addition nanotubes typically grew at perhaps 1% of catalytic sites for the growth procedures we have explored. To ensure a moderate probability of having a nanotube grown on a given tip, a large number (20 or more) of etched holes with catalytic particles could be fabricated. However, any given tip might have no tubes, one tube or several tubes.

Direct surface growth of SWNTs by CVD on catalyst-coated silicon tips has also been demonstrated, without the use of pores. We have analyzed approximately 300 tips prepared this way with scanning electron microscopy (SEM) and dozens of tips with transmission electron microscopy (TEM). As seen in Figure 1, we most commonly found densely coated tips with ropes and bundles of SWNTs extending from all sides of the silicon pyramid. These ropes often form complex loop structures not suitable for AFM work. About 1/3 of the tips examined had no tubes near the tip although they may have been covered by nanotubes elsewhere. Only a few percent of the probes had single nanotubes at the tip. Even fewer were oriented vertically.

The mechanical stability of the nanotubes directly grown on the silicon tips was found to be quite poor. As a control, we briefly imaged a smooth surface in tapping mode with tips having nanotubes at the end, as determined by SEM, before any attempts at electrical pulse shortening of the tubes. Afterwards, these probes were re-imaged by SEM. The nanotubes were lost from 7 of 9 tips used in this control experiment. It was also frequently observed during electrical pulse shortening that the tubes would fall off. The final yield of useful nanotube tips was therefore on the order of 1% of the number of originally fabricated probes using the direct growth method. While these results represent early attempts at developing nanotube AFM tips, and there was clearly significant progress possible with continued process development, we decided to focus on the technically simpler problem of developing suitable substrates for nanotube pickup.

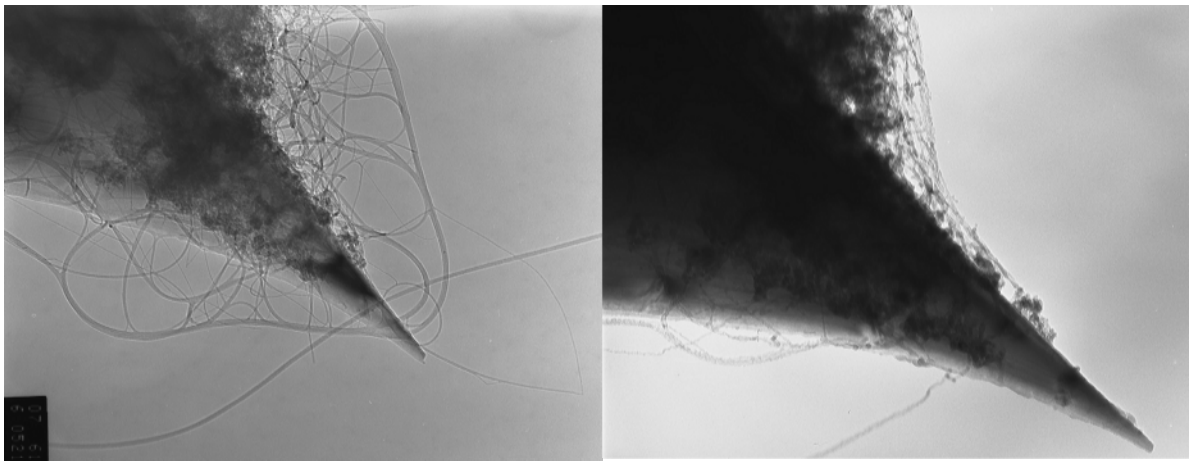

Figure 1. TEM images of nanotubes grown on AFM tip include ropes, multi-walled and single-walled tubes. Note that most of the growths consist of ropes.

Pick-up Substrate Preparation and Nanotube Growth

The pick-up technique is an efficient and consistent method for mounting SWNTs in the proper orientation. When SWNTs are grown on a flat substrate, a small percentage of the tubes are oriented vertically, and can be picked up when the AFM tip scans across the surface in tapping mode. Typically, 1 to 4 tubes can be picked up from a 10 μm square region. Given this tube density, a 6 mm substrate could in theory be used nearly a million times. Nanotube substrates suitable for pickup were produced using four methods of catalyst deposition and compared in side-by-side CVD growths. We achieved similar results with each of these techniques. The suitability of a substrate for nanotube pickup appears to depend primarily on the density and size distribution of the catalytic sites and not on how they were

deposited.

Pick-up of a nanotube is readily observed by monitoring the height signal of the AFM image while looking for a significant step change in the average position. The nanotube binds to the side of the pyramidal AFM tip via attractive van der Waals forces, and usually remains attached firmly enough that it can be repeatedly pressed into and scanned across the substrate surface. A picked up tube can be removed by holding the tip a few hundred nanometers above the substrate and applying a 50V, 100 μs pulse. The removal mechanism is not clear but probably involves either electrostatic attraction or ablation.

Nanotube pick up can reoccur several times, resulting in a 'bundle' of nanotubes attached to the tip. In figure 2, two bundles are shown that most likely were picked up sequentially, although it is possible that they grew this way on the substrate.

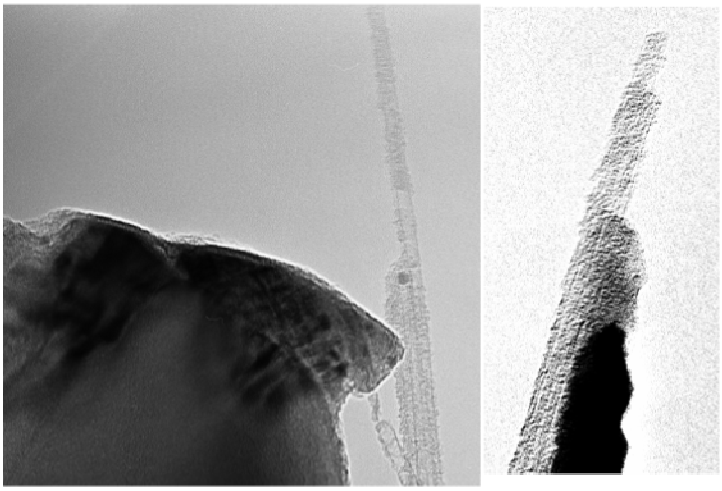

Figure 2. Several tubes have been picked up and stacked in 'bundles' on silicon AFM probes.

Silicon substrates were cleaved under cleanroom conditions, and cleaned by sonicating for 15 minutes at 25 ºC first in toluene, then in acetone, and finally in electronics-grade isopropyl alcohol. To coat the substrates with catalytic iron nanoparticles, 1-30 drops of 1-30 μg/mL $Fe(NO_3)_3 \bullet 9H_2O$ solution in electronics-grade isopropyl alcohol were applied while spinning substrates at 3000 r.p.m., waiting approximately 10 seconds between drops to permit the solvent to evaporate. We found that the catalytic sites would be considerably larger and often less homogeneously distributed over the surface at higher concentrations (e.g. 100-300 μg/mL $Fe(NO_3)_3 \bullet 9H_2O$). The nanotube growths on such substrates were correspondingly larger in diameter and sparser. Again, the critical factor is achieving a high density of very small catalytic sites.

Alternately, some silicon substrates were coated under high vacuum with ~1/40 monolayer of iron applied by thermal or electron beam evaporation. In general, the deposited catalyst sites were large and not optimal for SWNT growth. However, with continued development an optimal pickup substrate could most likely be fabricated via molecular beam epitaxy of the iron catalyst at patterned growth sites. Such a substrate can achieve a nearly uniform catalyst site size and therefore will grow a more uniform distribution of nanotubes; a high density of 1-3 nm diameter tubes with lengths less than 1 μm would be ideal. In addition, such a substrate is substantially more stable over time and can be used for nanotube pickup successfully for several years.

Other silicon substrates were incubated overnight at 4 ºC in a 44 μM solution of ferritin containing ~200 Fe atoms/protein, prepared as described by Dai and coworkers.[6] In this process, a calcination step is required after coating the substrate to remove all organic material originating from the ferritin protein, leaving behind only nanoparticles of iron oxide. This is done by heating the coated substrate in a furnace to 800 ºC in air and holding at that temperature for 10 minutes. This process gave the smallest catalyst size distribution and therefore yielded the most consistent nanotube growths. The catalytic site size distribution and the resultant growths were very consistent with those reported by Dai. The results from

a typical ferritin growth are depicted in Figure 3.

CVD growth was performed in a 22 mm inner diameter Lindberg/Blue M quartz tube furnace with a single heating zone 312 mm long. Five wafers are positioned 12.5 mm apart in a specially designed quartz holder, oriented vertically and with the catalyst coated side facing away from the direction of the incoming gas. A significant advantage of this holder is that it enables up to three small substrates to be mounted side-by-side in each slot for parallel comparison of growth results under nearly identical temperature and gas flow conditions. Optimal nanotube growth is obtained when the holder is positioned at the leeward end of the quartz tube, with the last wafer approximately 2 mm from the end of the heating zone.

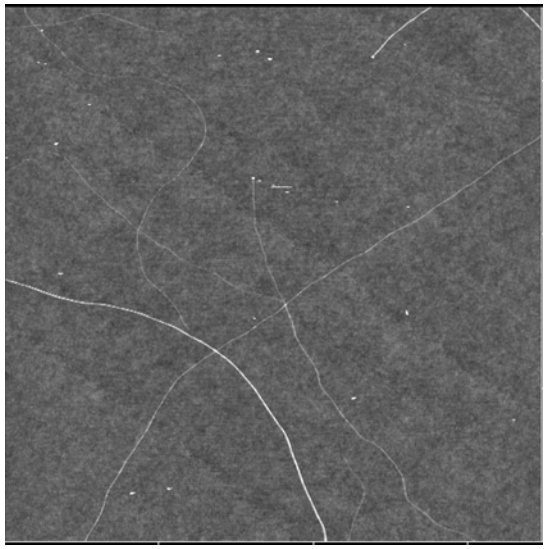

Figure 3. AFM height image of nanotubes grown from ferritin coated oxidized silicon substrate. Field of view is 3 x 3 μm. The height range is 10 nm.

The quartz tube is then flushed for 15 minutes with argon gas (Matheson, 99.9995% purity, 440 sccm). The furnace is heated at 950˚ C for approximately 20 minutes, and then held at 950˚C for 15 minutes, both under a flowing atmosphere of Argon (440 sccm) and H_2 (Matheson, research grade, 125 sccm). The furnace is held at this temperature for 5 additional minutes while being flushed with Ar (440 sccm). Growth of nanotubes is then carried out for 0.5 to 2 minutes at 950˚C with CH_4 (Air Liquide, Ultra High Purity, 1080 sccm) and H_2 (125 sccm). Following this growth step, the furnace is again flushed with Argon (440 sccm) and held at 950˚C before rapidly cooling to less than 250˚C, after which the substrates are removed from the furnace.

Substantial variations in growth density occurred between substrates mounted at different positions in the furnace or between identically placed substrates on different runs, which we attribute to temperature variations in the furnace. It was found that the substrate temperature could differ by as much as 20 ˚C with a 1 cm change in position in the furnace or upon changes in the gas composition and mass-flow. A three-stage furnace would likely help improve reproducibility.

Shortening AFM Nanotube Tips

Push and electrical pulse techniques for shortening nanotube AFM tips were examined individually and in combination. This was done on several different surfaces. The most efficient method was to combine pickup, pulse and push shortening all on a single substrate. Force calibration measurements were employed to establish the length of the nanotube tips using the method described by Cooper, *et al*.[5] This approach was found to be suitable for both push and electrical pulse shortening techniques. Once a nanotube has been picked up and shortened, the probe can be used for high-resolution imaging, biomolecular manipulations or force spectroscopy.

A general method for shortening utilizes electrical pulses.[2,7] The procedure to shorten the SWNT in air consists of applying +5 to +30 volt pulses of 20 to 100 μs duration between the AFM tip and a grounded, conductive substrate. Presumably the electrical pulse shortens the nanotube by ablation due to the very high electric field generated at the nanotube end. These pulses are supplied from a Hewlett-Packard 8114A pulse generator and routed to the tip through a Digital Instruments Signal Access Module, or “break-out” box, which is connected to the MultiMode AFM. The pulses are applied while tapping the surface at approximately 70 kHz or 300 kHz, which are the resonance frequencies of the

cantilevers we used (FESP and TESP cantilevers, Digital Instruments). While both work, we tend to prefer the softer FESP probes.

For a given SWNT tip, larger voltage pulses shorten the tube in larger increments, as do pulses of longer duration. But the voltage necessary to carry out shortening varies drastically between individual tubes. This is believed due both to the environmental conditions (especially humidity), and to the widely varying conductivities associated with nanotubes of slightly different molecular structure, for example, between semiconducting and metallic nanotubes. Nanotubes can be shortened precisely with steps as small as 2 nm per pulse. The main drawback to this technique is that the nanotube length removed can vary significantly from one pulse to another and one day to another. Hence to successfully employ this technique one must be careful and attentive. A secondary drawback is that electrical pulsing can dislodge the nanotube electrostatically from the AFM tip. Nevertheless, this second effect can also be exploited to controllably deposit nanotubes precisely on substrates for device fabrication.[8]

Push shortening of short, <100nm long tubes is accomplished by taking successive tip-substrate distance-sweep measurements, and incrementing the sweep start point by ~5 nm at a time.[9] By doing this, the tube can be pushed up along the tip. We find electrical pulse shortening to be more effective than push shortening in terms of being able to shorten a nanotube significantly (e.g. by several hundred nm in 20 nm steps).

For substrates with tubes of significantly varying length that are typically too long the combined approach, pulse shortening followed by push shortening has significant advantages. We have avoided the need for multiple substrates or a patterned substrate that includes pickup and separate shortening regions by reducing the field-of-view to ~10 nm during shortening.

Once the nanotube probe has been shortened to a useful length, the field of view can be increased to 100-500 nm so that a nanotube laying flat on the substrate can be imaged. An AFM image of a horizontal nanotube is a very good way to determine the quality of the final probe. Keeping the field of view small minimizes the chance that another nanotube is picked up.

Imaging with Nanotube Probe Tips

Table 1 in the manuscript lists the properties of 14 nanotube probes that were determined by TEM-AFM correlations described in the text. We have found that topographic image resolution when using SWNT probes was more sensitive to imaging conditions, particularly oscillation amplitude, than conventional silicon probes. This may be due to the small interaction area and compressibility of SWNTs. In addition, in about a third of the cases, the observed AFM resolution was significantly better than would be predicted from the nanotube probe diameter. We have also found that, at a given oscillation amplitude, a small change in drive frequency or in amplitude setpoint can improve image resolution when compared with the optimal settings used for imaging with a bare silicon probe. In particular, the amplitude set point for a nanotube probe can often be as high as 95% of the free oscillation amplitude in air and still permit high resolution imaging. A high amplitude setpoint corresponds to small tip-sample forces, which is desirable for imaging delicate biological macromolecules.

When imaging with SWNT tips in tapping mode AFM, care must be taken to recognize imaging artifacts. Imaging artifacts can be introduced through bending and thermal vibration.[10] In addition, buckled nanotubes frequently demonstrate degraded resolution or artifacts. We have also seen multiple tubes at the tip of some probes, either bundled together to form a “broom”, or attached to different faces of the silicon AFM tip oriented at an angle relative to one another. The data in table 1 of the main paper show that high resolution imaging without artifacts was only accomplished with probes consisting of single tubes that had not been previously buckled.

The TEM images also show the presence of a low density contaminant coating on the probes. Evidence suggests that this material is deposited by silicone oil outgassing from the "gel-pack" in which most of the probes were stored.[11] This is supported by the significant amount of movement of this contaminant over the nanotube observed during TEM imaging. We have found via TEM imaging that gel-free clamshell tip wafer enclosures deposit about an order-of-magnitude less contamination on silicon AFM probes than gel-pack enclosures. This will be important for those wishing to perform dip pen nanolithography or nanotube probe functionalization. However, the contaminant had a limited effect for AFM imaging in air.

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